

ELECTROCATALYTIC OXIDATION OF REACTIVE BLUE 198 USING Sm³⁺ DOPED CERIUM OXIDE AS A CATALYST

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Abstract

The nanoscience and nanotechnology have brought with new chance for new applications of some traditional pollution treatment technology. A part of new instance, in a rare earth doped cerium oxide nanopowder was used as a catalyst to investigate the removal of color and TOC from simulated wastewater of C.I. Reactive Blue 198. Graphite electrode was used as anode and cathode and electrolysis were carried out in presence of an electrolyte NaCl with a catalyst concentration of 50 mg/L at a constant current density of 34.96 mA/cm². In order to find the efficiency of nanocatalyst, experiments were also conducted without catalyst. From the experiment, it was found that complete color removal was achieved on electrocatalytic oxidation as well as electro oxidation process. When comparing the above processes, catalytic oxidation shows more efficiency than electro oxidation. Under the same experimental condition the removal of TOC was found to be 24% for electro oxidation and 46% for electro catalytic oxidation. It infers that even though the electro-catalytic oxidation process achieves complete decolorization but it does not achieve complete mineralization. The UV-visible spectrum confirms the decolorization and FTIR studies confirmed the changes in the functional groups after treatment.

Key words: Electrocatalytic oxidation; Reactive Blue 198; Sm³⁺ Doped cerium oxide; Graphite electrode; Color removal.

I. INTRODUCTION

The growth of industries and day-to-day changes in human activities has resulted in an increase in the volume and complexity of wastewater to the environment. The textile industry is one of the most polluting industries in terms of discharge volume and effluent composition [1]. Reactive dyes represent an important fraction of the commercialized synthetic dyes used (approximately 12% of the worldwide production) [2]. The main environmental problems associated with the reactive dyes are their low exhaustion. Frequently, the fixation efficiency of these dyes range between 60% and 90% [3]. Dye bath effluents are not only aesthetic pollutants by their color but also interfere with light penetration that disturbs biological processes. Furthermore, dye effluent may contain chemicals that are toxic, carcinogenic, mutagenic or teratogenic for microbes and fish species [4]. Color is usually the first contaminant to be recognized in wastewater and a very small amount of dye in water is highly visible and affects, water transparency and gas solubility of water bodies. The treatment of wastewater containing dyes and its decolorization involves serious problems, such as lower efficiency in color removal and mineralization [5]. However, methods adopted in industry concentrate the dye pollutants and necessitate secondary treatment.

On the other hand, degradation involving biological processes is not efficient as the synthetic dyes in the effluent are highly structured polymers with low biodegradability [6].

Electrochemical oxidation is emerging as a strong alternative for wastewater treatment because several industrial processes generate toxic wastewaters which are not easily biodegradable and require costly physical or physico-chemical pretreatments [7]. Many researchers have investigated the electrochemical oxidation for various types of effluent [8]. However, more recently the electrocatalytic oxidation technique has been developed by chemical and environmental engineers. This technique is particularly advantageous as it provides high pollutant degradation, easy control and low cost [9]. The key role of the electrocatalytic process is the electrode material, and many materials have been examined such as SnO₂, PbO₂ and boron doped diamond (BDD) [10].

“Metal nanoparticles” receive much attention because of their uniform size and sharp size distribution in nanometers, and because they are easily prepared as a result of recent developments in nanoscience and nanotechnology. In addition, catalysts based on such metal nanoparticles are highly active and selective.

They also exhibit a long lifetime for several kinds of chemical reactions [11,12]. Rare earth salts are converted to rare earth oxides during the calcination process, and these oxides were uniformly adsorbed on the surface of ceria. Balazs and Glass [13] reported that the ionic radius of the dopant did not affect the conductivity of ceria. Gadolinium (Gd) and samarium (Sm) are considered as the most effective dopants for ceria in terms of maximization of the ionic conductivity [14].

In this study, C.I. Reactive Blue 198 (RB 198), as a model contaminant was used, for investigating the efficiency of electro oxidation and electro catalytic oxidation using samarium doped cerium oxide as a catalyst. The characteristic absorption bands of RB 198 at 625 nm were investigated through UV-visible spectroscopy, and mineralization was observed by total organic carbon (TOC) analysis. The changes in functional group during the process were verified by FTIR techniques.

II. MATERIALS AND METHODS

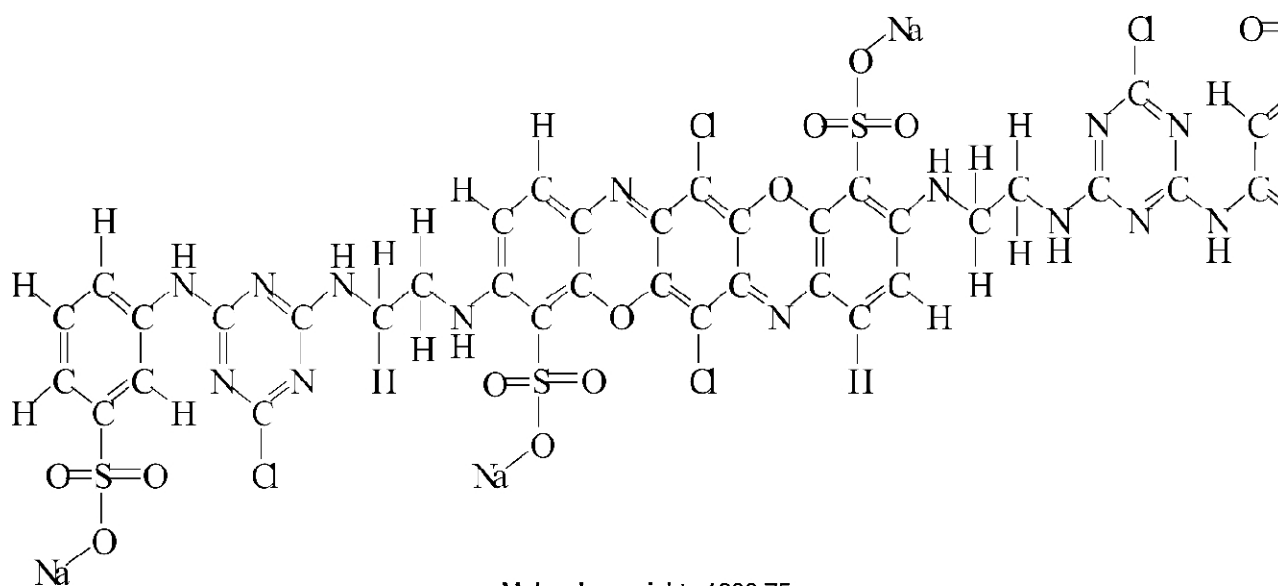
A. Chemical reagents

Reactive dye C.I. Reactive Blue (RB 198) CAS No: 124448-55-1 was obtained from Jansons International Ltd., Mumbai, India. The properties and

chemical structures of the dye are given in Fig. 1. Samarium doped cerium oxide were obtained from the University of Concepcion, Chile. The preparation of the nanomaterial is shown by Mangalaraja *et al* [15]. Analytical grade hydrochloric acid, sodium chloride and sodium hydroxide (Loba chemie, Mumbai, India), Potassium bromide (Sigma-Aldrich) were used in this study. The graphite materials used were obtained from M/S Carbone Lorraine, Chennai, India. The pH of the aqueous sample was adjusted by adding 0.1 N HCl and 0.1 N NaOH and analyzed before and after treatment using a pH meter (Susima pH meter AP-1 Plus, Chennai, India). All the solutions were prepared using deionized water.

B. Experimental setup

The experiments were conducted by batch process using 250 mL capacity of the batch reactor under constant current density of 34.96 mA/cm^2 and 50 mg/l catalyst of samarium doped cerium oxide was added in suspension of the synthetically prepared wastewater. It was prepared by dissolving RB 198 in double distilled water at a concentration of $650 \mu \text{ M}$. The experiments were carried out as per the optimum conditions obtained from our preliminary study. The experimental setup used in this study was same as those in the previous work [8]. The graphite anode and



Molecular weight: 1288.75

Molecular formula: $\text{C}_{40}\text{H}_{26}\text{Cl}_4\text{N}_{14}\text{O}_{14}\text{S}_4\text{Na}_4$

Fig. 1. Chemical structure and molecular weight for C.I. Reactive Blue 198 (RB 198)

cathode were positioned vertically and parallel to each other with an inter gap of 8mm to reduce the ohmic losses and superficial graphite surface of working electrodes each having $6.5 \text{ cm} \times 5.5 \text{ cm}$ with contact surface area of 71.5 cm^2 . The solution was constantly stirred using a magnetic stirrer (Superfit, Coimbatore, India) in order to keep its contents well mixed during the experiment. The electric power was supplied with regulated DC power supply and fixed current 2.5 A (Sri Sai Scientific, Coimbatore, India).

C. Analytical techniques

All the experiments were carried out at pH 7 and NaCl concentration of 0.13 M. The aqueous solutions resulting from electrocatalytic oxidation treatment were analyzed after filtering the sample by $0.45 \mu\text{m}$ cellulose acetate glass filter. Colour removal was monitored using a double beam UV-vis spectrophotometer (UV- Shimadzu 3600, Japan) and organic removal by analyzing TOC (Shimadzu TOC-V_{CPH} model, Japan). For FTIR, the sample was filtered, and air-dried to a constant weight for analysis (IR Nicolet 10, USA).

III. RESULTS AND DISCUSSION

A. UV-Visible spectroscopy

The comparison of UV-Vis spectra of Reactive Blue 198 aqueous solutions before and after 20 min of electro oxidation and electrocatalytic oxidation are presented in Fig. 2. Both processes were performed at the optimal conditions which were chosen after preliminary studies. The spectra of dye initial solution represent UV bands characteristic for chromo group at 297 nm are related to the benzene rings bonded. The dramatic changes of UV spectra represent a disappearance of both chromo group and aromatic groups during the degradation of Reactive Blue 198 dye. Electrocatalytic treatment appears much more efficient than electro oxidation process. It can be seen in Fig. 2 (a) that, the optimum condition of electrochemical oxidation processes, a rapid decrease in chromo group during first 5 min, but electrolysis time increased upto 20min, there are some residues present after oxidation processes. However, Fig. 2 (b) shows the gradual decolorization of reactive dye in aqueous solution using Samarium doped cerium oxide nanoparticles in electrocatalytic oxidation process and achieved complete decolorization. The reason for such degradation process may be due to catalyses of

samarium doped cerium oxide into an oxygen atom, eventually yielding more hydroxyl radicals, can enhance the degradation of Reactive Blue 198.

It can be observed that the peaks decrease gradually with time, indicating that chromophore of RB 198 is broken and decolorized. Even though, chromo group is removed in both cases. The formation of new peak at 297 nm at the end of the electrolysis shows that the mineralization of the RB 198 is not completely achieved. The decrease of absorbance at 297 nm was indicative of the aromatic ring degradation [16]. This peak may be attributed to carboxylic acids accumulated at the final stage of the oxidation. This indicates that residual TOC are present in the effluent.

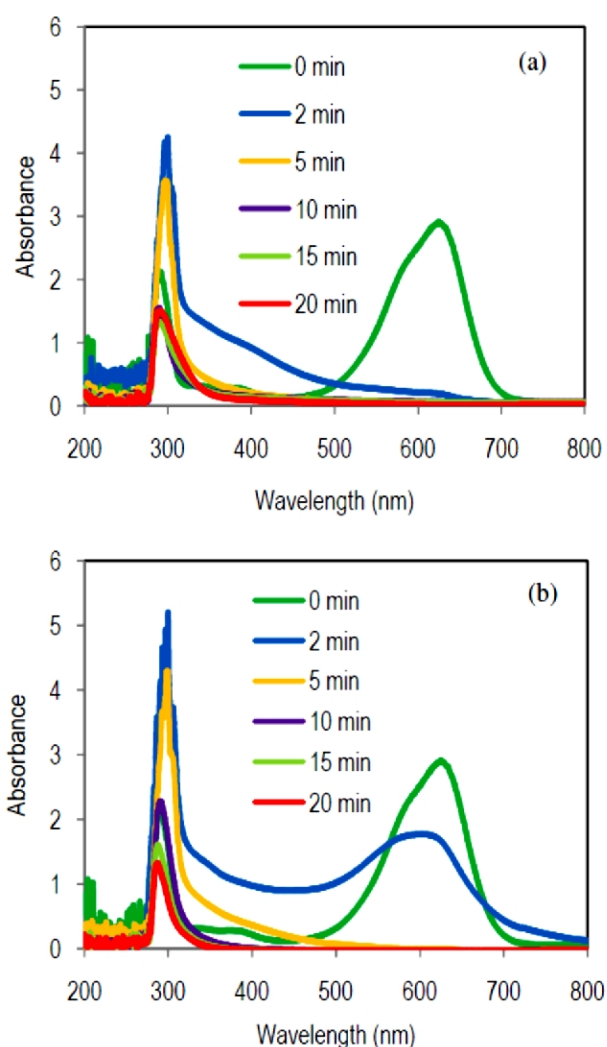


Fig. 2. UV-V is spectra changes of Reactive Blue 198 during electro oxidation (a) and electrocatalytic oxidation (b)

B. Mineralization studies

The comparative effects of electro oxidation and electro catalytic oxidation on the changes of TOC in aqueous solutions of Reactive Blue 198 dye is presented in Fig. 3. The results in Fig. 3 indicated that the percentage of TOC values were about 24% during electro oxidation and 46% on electrocatalytic oxidation treatment. The results of TOC analysis indicate that organic compounds are not completely oxidized to CO₂ and water. For example, in the case of RB 198, only 24% of mineralization was obtained in the electro oxidation, when Ce_{0.8}Sm_{0.2}O₂ was used as catalyst, addition of electro oxidation is beneficial (22% mineralization in 20 min). Moreover, the contrasting effect of chloride ions on the color and TOC removal indicates that the electrogenerated active chlorine and •OH species are quite selective for the oxidation of the chromophore of the dyes.

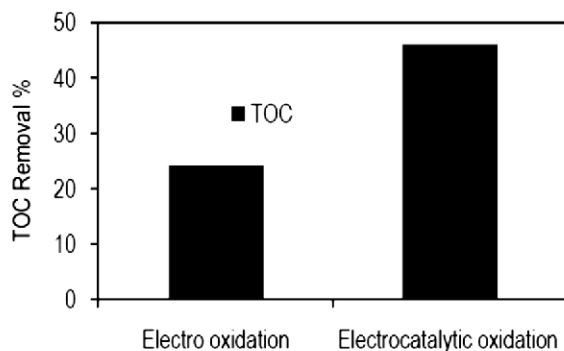


Fig. 3. TOC removal by electro oxidation and electrocatalytic oxidation of RB 198

The electrochemical decoloration of dyes is well documented in the literature and is believed to involve •OH radicals which are produced in a series of reactions. These radicals then attack the dye molecule and cause it to degrade [17]. In cases where electro oxidation process is low mineralization of the RB 198 is believed to be the result of fast decolorization of electrogenerated active species. On the other hand, nanocatalyst having certain transition metal ions improves the electron trapping and inhibits electron-hole recombination [18]. In this case, the presence of transition metals increases the electrocatalytic activity either by scavenging electrons that reduces the recombination of charges and therefore favors the •OH formation, or by modifying the

surface properties of the material regarding the active sites, presence of defects, etc., which eventually increases the adsorption and favors the interfacial reactions.

C. FT-IR studies

Figure 4 illustrates the FTIR spectra of RB 198 before and after 20 min of electrolysis. Fig. 4 (a) shows the several bands can be distinguished in the spectra. The broad peak around 3442.84 cm⁻¹, which assigns to N-H vibration [19]. Furthermore, the peaks at 2929.47 cm⁻¹ and 2856.84 cm⁻¹, which represent the C-H symmetric stretching and C-H asymmetric stretching of CH₂, respectively [20]. The vibrations located at 1607.10 cm⁻¹ (a combination of phenyl ring vibrations with stretching of the C = N group), can be observed the band at 1547 cm⁻¹, which were associated with the chromophore of the reactive dye, 1413.66 cm⁻¹ (O-H bending vibrations), and 1127.89 cm⁻¹ (symmetric vibrations of the sulfonate groups). The peaks at 1035.52 cm⁻¹ and 795.52 cm⁻¹ account for Cl. The peaks at 616 cm⁻¹ account for aromatic or benzene ring. Figure 4 (b) spectrum of Samarium doped cerium oxide is very difficult to assign the behavior of the peaks but shows few interesting regions. The first in the range 3000-3750 cm⁻¹ with a maximum at 3423 cm⁻¹, arises from the absorption of O-H groups. The second region in the range 1250-1750 cm⁻¹, originates from the absorption of COO⁻ (1581 cm⁻¹). Surprisingly, the peak at 2362.4 cm⁻¹, typical of CO₂. It is difficult to assign the behavior of Samarium doped cerium oxide by FTIR spectra as stated earlier by Kannan and Mohan [21] in which the appearance of peaks were observed at around 1200 cm⁻¹ to 400 cm⁻¹. But the observed spectra for Sm³⁺, seems to be a noise pattern rather than the transmitted intensity pattern.

Figure 4 (c) represents after 20 min of electro oxidation the FTIR spectrum was obviously modified with respect to the aforementioned spectrum of the initial working dye. It can be observed that the bands at 3457.88 cm⁻¹ which indicate the presence of both free and hydrogen bonded OH groups. The peak becoming weaker near 1631.55 cm⁻¹, which is responsible for the combination of stretching vibration of C=O conjugated with C=C [22]. The peaks at 2929.47 cm⁻¹, 2856.84 cm⁻¹, 1547.10 cm⁻¹, 1413.66 cm⁻¹, 1035.52 cm⁻¹ and 795.52 cm⁻¹ get completely disappeared. Furthermore, a new absorption peak of

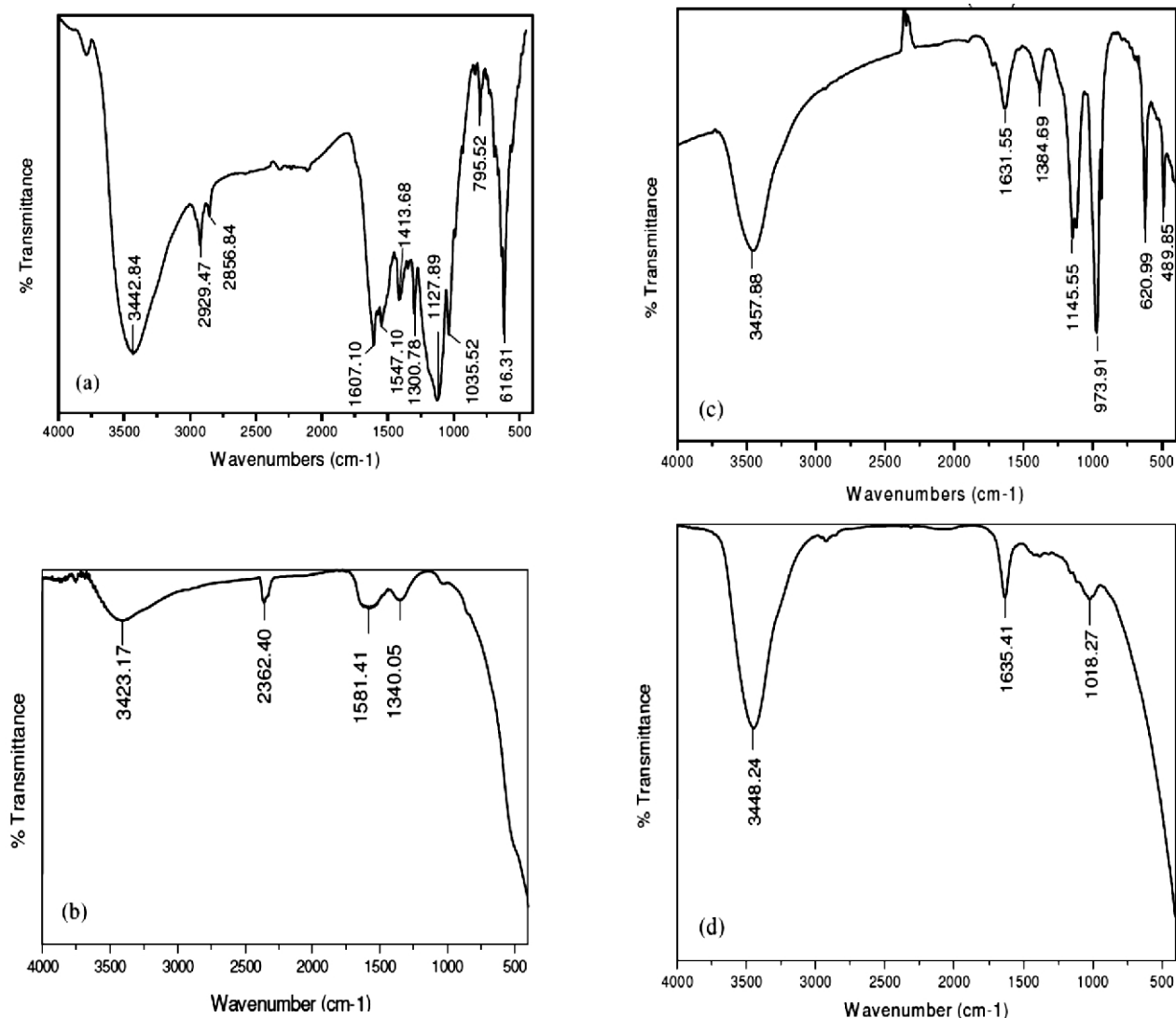


Fig. 4. FTIR spectrum of the Reactive Blue 198 powder (a), Samarium doped cerium oxide (b), after electro oxidation (c) and after electrocatalytic oxidation (d)

1631.55 cm⁻¹ was observed, which can be assigned as the stretching of C=O in carboxylic groups, aldehydes or ketones [23] generated in the process.

The presence of this band indicated the formation of new species, which originated from the fragmentation of the parent RB 198 molecule. The formation of new peaks at 1145.31 cm⁻¹ and 975.52 cm⁻¹ indicates the C-NO₂ of aromatic ring and C-N stretching of aromatic NO₂. After 20 min of electrocatalytic oxidation (Fig. 4 (d)), the frequencies of the vibration modes change either. The peaks at 1341, 1141 and 973 cm⁻¹ completely disappeared and hence in moreover, there were clear differences between the relative intensities.

Compare the efficiency of electro oxidation and electrocatalytic oxidation process, catalytic oxidation shows the maximum degradation of organic content compared to electro oxidation. This variation in the FTIR spectra has clearly explained the incomplete mineralization of RB 198 dye.

IV. CONCLUSIONS

In this study, the electro oxidation and electrocatalytic oxidation of Reactive Blue 198 have been investigated. The rare earth oxides - samarium doped cerium oxide was used as a catalyst for electrocatalytic oxidation. The degradation of high concentration and high-chroma of RB 198 is completely

decolorized through the electro oxidation electrocatalytic oxidation process. During electro oxidation process after 20 min, the removal of colour and TOC were found to be 99% and 24% respectively, and 100% and 46% respectively for electrocatalytic oxidation process. The novel approach of combining samarium doped cerium oxide is effective for the removal of pollutants from textile dye wastewater in short durations.

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